The Temperature Dependence of ln*K*

<u>van't Hoff equation</u>: $\dfrac{d\ln K}{dT} = \dfrac{\Delta H_r^o}{RT^2}$

What if we can't assume that ΔH_r^o is independent of T?

Recall: $\Delta H_r^o(T) = \Delta H_r^o(T=0) + \int_0^T \Delta_r C_p$ (assuming no phase changes)

where $\Delta_r C_p = \sum_i^{N_s} \nu_i C_{p,i}$

and in general, $C_p = a + bT + cT^2 + \cdots$ and then $\Delta_r C_p = \Delta a + \Delta bT + \Delta cT^2 + \cdots$.

(and $\Delta b = \sum_i^{N_s} \nu_i b_i$, etc.)

Then:

A. $\Delta H_r^o(T) = \Delta H_r^o(T=0) + \Delta aT + \frac{1}{2}\Delta bT^2 + \frac{1}{3}\Delta cT^3 + \cdots$

and: $d\ln K = \dfrac{1}{RT^2}\left[\Delta H_r^o(T=0) + \Delta aT + \frac{1}{2}\Delta bT^2 + \frac{1}{3}\Delta cT^3 + \cdots\right]dT$

integrating:

B. $\ln K = -\dfrac{\Delta H_r^o(T=0)}{RT} + \dfrac{\Delta a}{R}\ln T + \dfrac{\Delta b}{2R}T + \cdots + I$

where *I* is a constant of integration

Notes:

(1) if $\Delta H_r^o(T)$ is known for <u>any</u> one temperature (perhaps 298 K) and $C_p(T)$ is known for each reactant and product, then $\Delta H_r^o(T=0)$ can be calculated (eqn. A).

(2) if $\Delta H_r^o(T=0)$ is known for the reaction and *K* is known for <u>any</u> one temperature, *I* can be evaluated (eqn. B).

(3) Then K can be calculated at <u>any</u> temperature.